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THE ISOLATION OF MESITYLENE, PSEUDOCUMENE, AND HEMIMELLITENE FROM AN OKLAHOMA PETROLEUM [1]

By Beveridge J. Mair [2] and Sylvester T. Schicktanz [2]

ABSTRACT

Mesitylene, pseudocumene, and hemimellitene have been isolated in very pure condition from a midcontinent petroleum. This has been accomplished by extracting with liquid sulphur dioxide the fraction distilling from 118° to 132° C. at 215 mm and fractionally distilling and crystallizing the extract. Selective sulphonation and crystallization of the sulphonic acids and their hydrolysis have also been employed. The boiling points, freezing points, refractive indices, densities, and infrared absorption spectra of these hydrocarbons have been measured. Mesitylene was found to have two crystalline modifications melting at −44.78° and −51.74° C., respectively.

The content of pseudocumene and hemimellitene in the crude petroleum was about 0.2 and 0.06 percent, respectively. The amount of mesitylene in the fraction extracted was about 0.02 percent of the crude. More mesitylene, however, may be expected in the lower boiling fractions.

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INTRODUCTION

The occurrence of mesitylene (1, 3, 5-trimethylbenzene) and pseudocumene (1, 2, 4-trimethylbenzene) in petroleums of widely different origin has long been well established. LaRue and Müller (1)[3] in 1856 prepared the "sulphocumolate of barium" (probably the barium salt of pseudocumenesulphonic acid) from a Burma

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[2] Research associate representing the American Petroleum Institute.

[3] Arabic numerals in parentheses here and throughout the text relate to the bibliography at the end of this paper.

petroleum. Engler (2) succeeded in separating the trinitro derivatives of mesitylene and pseudocumene by crystallization from hot alcohol, and by using this method on petroleums of different origin established the almost universal occurrence of these hydrocarbons. Markownikoff (3) established the presence of pseudocumene in a Caucasian petroleum by purifying the sulphonic acid, converting it into the corresponding acid chloride and amide, and determining the melting points of these derivatives. He also established the presence of mesitylene by crystallizing the nitro derivative from hot alcohol. Many other investigators (4) have established the presence of mesitylene and pseudocumene. All, however, used similar methods for proving the identity of the hydrocarbon, namely, isolation of a small quantity of one or more solid derivatives and measurement of its melting point.

The presence of hemimellitene (1, 2, 3-trimethylbenzene) in petroleum appears to have escaped detection until now.

Although rough estimates of the total quantity of mesitylene and pseudocumene in certain fractions of petroleum are available (2), based on the total nitro compounds isolated, no one appears to have separated the three trimethylbenzenes from each other and estimated their amounts in a particular petroleum.

This paper contains a description of the isolation of these hydrocarbons in a pure state by physical and chemical methods and an estimation of the amounts present in an Oklahoma petroleum (5).

II. DESCRIPTION OF THE FRACTION CONTAINING THE TRIMETHYLBENZENES

The petroleum, after a preliminary distillation in an oil refinery, was further fractionated with the aid of efficient rectifying columns (6), the final distillations being performed at a pressure of 215 mm. At this pressure, the fraction containing the trimethylbenzenes distilled from 118° to 130° C., which corresponds approximately to 162° to 174° C. at 760 mm. The distribution by volume of this fraction with respect to boiling range is shown in figure 1. The total volume of this fraction was 35,120 ml. This was combined with 5,050 ml of mother liquors of the fraction from which *n*-decane had been removed by equilibrium melting (7). Before the removal of *n*-decane this fraction distilled between 169.5° and 175° C. The volume and approximate boiling range at 215 mm of this fraction are shown by the shaded block in the lower right corner of figure 1. The high refractive indices of the *n*-decane mother liquors ($n_D^{20}=1.45$–1.46) indicated the presence of aromatics. The refractive indices of the rest of the fraction (a maximum of $n_D^{20}=1.452$ at 125° to 126° C. and minima $n_D^{20}=1.439$ at 118° to 119° C. and $n_D^{20}=1.436$ at 129° to 130° C.) were also higher than could be accounted for by the paraffins and naphthenes boiling in this region and suggested the presence of aromatics.

III. EXTRACTION WITH SULPHUR DIOXIDE AND DESCRIPTION OF THE SULPHUR-DIOXIDE EXTRACT

The 40-liter combined fraction described above was extracted with liquid sulphur dioxide at −35° to −50° C., in an extractor previously used for the isolation of the xylenes (8). Both the miscible

and immiscible portions were left standing over night in open vessels to allow a considerable portion of the sulphur dioxide to evaporate. The fractions were washed with a solution of sodium carbonate, then with water, and finally dried with anhydrous calcium chloride. The immiscible fraction was again fractionally distilled and the portions with high refractive indices again extracted.

The miscible portion was finally distilled once in the very efficient columns packed with jeweler's locket chain (9). The distribution by

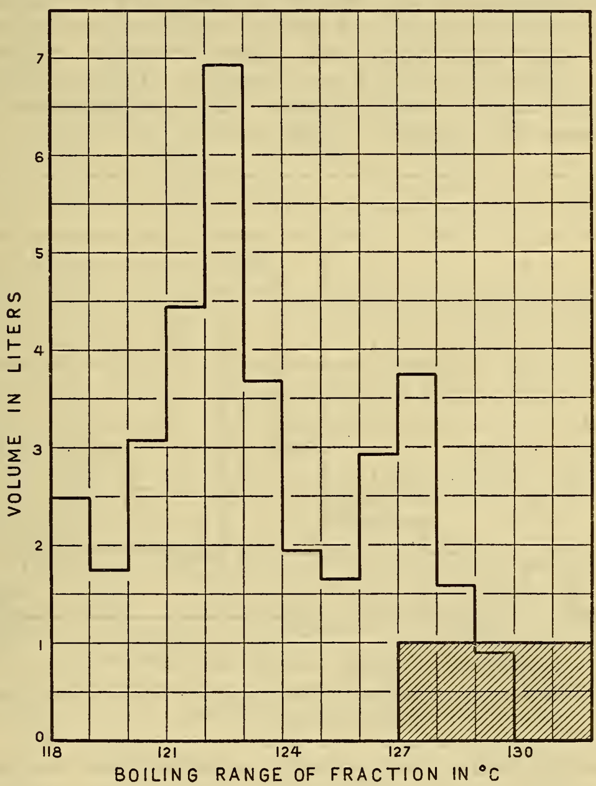

FIGURE 1.—*Distribution by volume of the fractions with respect to boiling range at 215 mm.*

volume of the miscible portion with respect to boiling range is shown in figure 2. The total volume of this distillate was 9,537 ml.

The refractive indices of these fractions ranged from the low value $n_D^{20}=1.456$ for the fractions distilling around 119° C. to the value $n_D^{20}=1.502$ for the fractions distilling between 125° and 126° C. The indices then decreased to $n_D^{20}=1.486$ at 127.5° C. and rose again to a maximum of $n_D^{20}=1.5116$ around 130° C. Crystals could be obtained only with difficulty from the fractions distilling below 123° C. because these became very viscous or glassy on cooling. In other fractions crystals appeared at from −90° to −120° C. The temperature at which crystals appeared rose from −73° C. for the fraction distilling at 123° C. to −50° C. for that distilling at 126° C. In the distillation range 126.5° to 127.5° C. the fractions became glassy.

Crystals again appeared in the distillates from 128° to 132° C., the maximum freezing point, −33° C., coinciding with the high refractive index $n_D^{20} = 1.5116$ for the fraction distilling at 130° C.

In addition to the sulphur-dioxide extract just described, a further aromatic fraction was obtained by treating the immiscible portions with concentrated sulphuric acid. The fractions were stirred vigorously at room temperature for 22 hours with one fourth of their volume of 100 percent sulphuric acid. The sulphuric acid layer was run into ice and the hydrocarbons were regenerated by hydrolysis. This material was washed with sodium-carbonate solution, then with water, dried with calcium chloride, and fractionally distilled. A total of 1,030 ml was obtained. This material was kept separate until some pseudocumene and hemimellitene had been isolated from the sulphur dioxide extract by physical methods.[4]

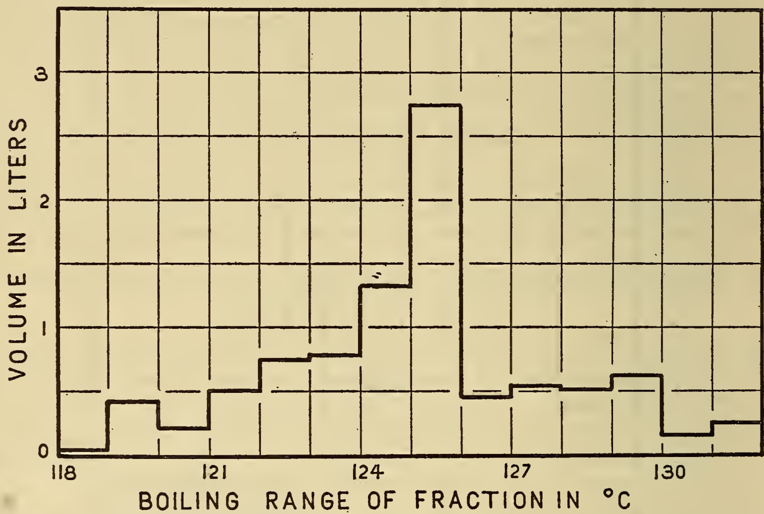

FIGURE 2.—*Distribution by volume of the sulphur dioxide extract with respect to boiling range at 215 mm.*

The trimethylbenzenes were finally isolated from the fraction obtained by sulphonation and hydrolysis by the same methods as those applied to the extract.

Some of the immiscible fractions were treated a second time with sulphuric acid. Since these showed no change in refractive index on this treatment, it was concluded that the aromatics had been completely removed and the fractions were reserved for the isolation of their other constituents.

[4] Baeyer (10) has shown that some of the hydrogenated aromatics on treatment with a nitric-sulphuric acid mixture yield nitro compounds of the atomatics. The extra hydrogen atoms apparently are oxidized. White and Rose (11) at this Bureau have confirmed this by obtaining nitromesitylene from 1, 3, 5-trimethylcyclohexane. The objection might consequently be raised that the isolation of the nitro compound, or any derivative where a strong oxidizing agent has been used, does not necessarily prove the existence of the aromatic itself. This objection is not valid for the trimethylbenzenes in the case of a petroleum which has been effectively fractionated by distillation and in which a narrow fraction 160° to 175° C. is used, since the trimethylcyclohexanes boil 15° to 20° C. lower. Another possible objection concerns the Jacobsen rearrangement. Jacobsen (12) has shown that durene and the pentamethylbenzenes undergo a rearrangement on treatment with concentrated sulphuric acid and that trimethylbenzenesulphonic acids are produced from durene. Since durene boils at 195° C., it is not likely to be present in the 160° to 175° C. region of a carefully fractionated petroleum.

IV. ISOLATION OF PSEUDOCUMENE BY PHYSICAL METHODS

From a consideration of the properties of the distilled extract described in the preceding paragraph, it was obvious that at least two aromatic hydrocarbons were present. The presence of pseudocumene was suspected in the region from 123° to 126° C. and of hemimellitene in that from 128° to 132° C. The isolation of pseudocumene was attempted first. Purification by equilibrium melting with the use of a centrifuge designed for low temperatures (13) gave only fair results. For example, it was possible to split up a fraction with index $n_D^{20}=1.5016$ into three nearly equal portions with the following indices: $n_D^{20}=1.5030$, 1.5014, 1.5007. It was obvious that the isolation of all the pseudocumene by this method would be a very tedious procedure. Further fractional distillation did little to improve the purity of this material. The removal of nonaromatic material was evidently desirable, but further extraction with sulphur dioxide was impractical, because fractions with index above 1.46 were almost completely miscible.

Tausz and Stüber (14) have devised a method which removes the bulk of nonaromatic material from a sulphur dioxide extract. These investigators worked with the toluene and xylene fractions of an Edeleanu sulphur dioxide extract from a refinery. This extract contained about 50 percent of nonaromatic hydrocarbons. If this material was shaken with liquid sulphur dioxide and petroleum ether at low temperatures, it was found that the petroleum ether layer contained the bulk of the nonaromatic hydrocarbons together with some of the atomatics, while the sulphur-dioxide layer consisted almost entirely of aromatics and petroleum ether. By repeating this process a number of times, these investigators found that it was possible to get a sulphur-dioxide layer which contained only aromatics and petroleum ether. A low-boiling petroleum ether was used so that it could be separated readily from the aromatics by distillation.

This method was found useful in the isolation of pseudocumene but was applied in a manner somewhat different from that used by Tausz and Stüber (14). In the following description the letters *A*, *B*, *C*, etc., refer to figure 3, in which the various steps in the isolation of pseudocumene and mesitylene are depicted. Portions of the distilled extract were mixed with twice their volume of low-boiling petroleum ether and run through the extractor at −40° C. (*A*). The petroleum ether was removed from the immiscible portion by distillation. The aromatic hydrocarbons in this portion had now decreased sufficiently so that it could be run through the extractor without the admixture of petroleum ether (*B*). The miscible portion thus obtained was then extracted after admixture with petroleum ether (*C*). The combined extracts were treated as before to remove sulphur dioxide and dried (*D*). They were then fractionally distilled (*E*). It was evident from the rise in the refractive indices that the greater part of the nonaromatics had been removed by this treatment.

Equilibrium melting and centrifuging were again applied to the fractions with indices above 1.50, which distilled between 124° and 126° C. (*F*). The fractions were, however, viscous at their freezing point and, as previously mentioned, only a fair separation was obtained. By mixing the fraction with 30 to 40 percent of dimethyl

ether,[5] the viscosity of the liquid was considerably diminished, and the texture of the crystals was improved. White, dry crystals were obtained on centrifuging. These crystals were wetted with a small quantity of dimethyl ether and again centrifuged. This method was about three times as effective as crystallization without a solvent.

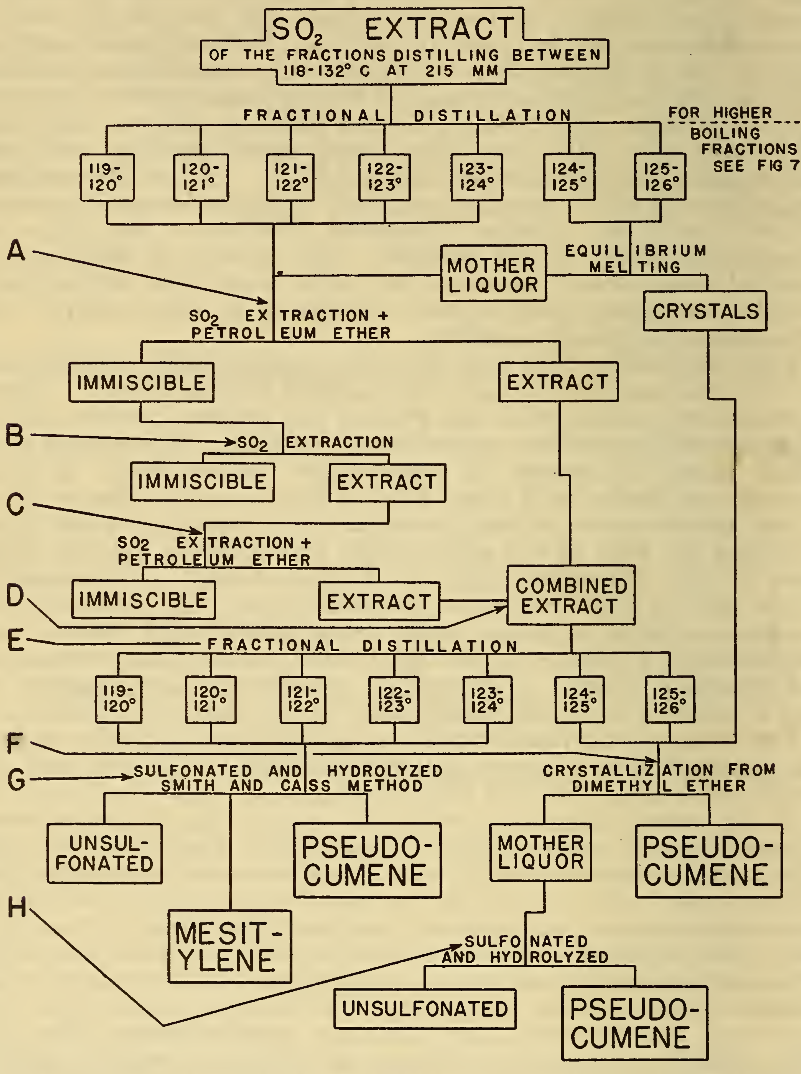

FIGURE 3.—*Chart showing the steps in the isolation of pseudocumene and mesitylene.*

The dimethyl ether was removed from the mother liquor by distillation and used over again. Before determining the physical constants of the crystal fraction, the last traces of dimethyl ether were removed by refluxing the sample for a few minutes in a long-necked flask. The pseudocumene thus obtained is listed in table 1 as "pseudocumene by physical methods."

[5] The dimethyl ether was furnished through the courtesy of E. I. duPont de Nemours and Co.

TABLE 1.—*Pseudocumene isolated from petroleum*

Method of isolation	Volume	Refractive index N_D^{25}	Freezing point in air	Purity
	ml		°*C.*	*mole, percent* [1]
Physical method	90	1.5025	−44.09	99.90
Do	610	1.5023	−44.6	98.56
Do	540	1.5015	−45.8	95.46
Do	340	1.5013	−46.6	93.44
By hydrolysis from mixtures with mesitylene	675	1.5022	−45.6	95.97
From mother liquors by hydrolysis	1,035	1.5025	−46.95	92.56

[1] The purity of the pseudocumene was calculated from equation (47), p. 203, E. W. Washburn, Principles of Physical Chemistry, McGraw-Hill Book Co., 1921. For the heat of fusion of pseudocumene the value 2,750 g-cal$_{15}$/mole determined by Rossini (15) was used. It was assumed that the freezing point of pure pseudocumene was 0.04° higher than that of the best sample recorded above.

V. SEPARATION OF PSEUDOCUMENE AND MESITYLENE

Two aromatic hydrocarbons are reported in the literature with boiling points immediately below that of pseudocumene. These hydrocarbons and some of their constants are recorded below:

	B.P.$_{760}$	M.P.	n_D^{20}
	°*C.*	°*C.*	
Tertiary butylbenzene	168.7	−58.1	1.4969
Mesitylene	164.6	−51.7	1.4992

The presence of one or both of these hydrocarbons together with pseudocumene was suspected in the fractions distilling between 119° and 124° C. The low refractive indices of these fractions, $n_D^{20} = 1.491$ to 1.499, were in accord with this suspicion. Since these fractions became very viscous and froze at very low temperatures, −80° to −120° C., it was decided to attempt their separation by sulphonation and hydrolysis rather than by fractional crystallization.

An excellent method for the separation of mesitylene and pseudocumene, depending on the hydrolysis of mesitylenesulphonic acid from constant-boiling hydrochloric acid at 80° C. and subsequent hydrolysis of pseudocumenesulphonic acid from sulphuric acid at 130° to 140° C., has been developed by Smith and Cass (16). This method was applied to the fractions distilling between 119° and 124° C. (*G*, fig. 3), yielding only mesitylene, pseudocumene, and nonaromatic material. The recovery was about 90 percent. The presence of tertiary butylbenzene was not detected.

VI. PSEUDOCUMENE FROM THE PSEUDOCUMENE MOTHER LIQUORS

The mother liquors from the fractional crystallization of pseudocumene previously described (*F*, fig. 3), with refractive indices n_D^{20} from 1.497 to 1.500, contained nonaromatic material as their principal impurity.

These mother liquors were sulphonated, and steam was passed through the solution of the sulphonic acids at 105° to 110° C. to

remove the unsulphonated material. After this had been removed, more sulphuric acid was added and the pseudocumene hydrolyzed at 130° to 140° C. (*H*, fig. 3). The amount of pseudocumene thus obtained is listed in table 1.

VII. PHYSICAL CONSTANTS OF PSEUDOCUMENE

Values of certain physical constants for the best pseudocumene isolated from petroleum are compared in table 2 with values for synthetic material recorded in the literature. The agreement, although not perfect, establishes the identity of the hydrocarbon isolated from petroleum as pseudocumene. The density was determined by the Capacity and Density Section of this Bureau. The refractive index was measured with a calibrated Abbé refractometer (Valentine design) at 25.0 ± 0.1° C.

The freezing and boiling points were determined with a platinum-resistance thermometer and accessory apparatus described elsewhere (17). The first few attempts to determine the freezing point were not satisfactory. Fluctuations in temperature readings as great as

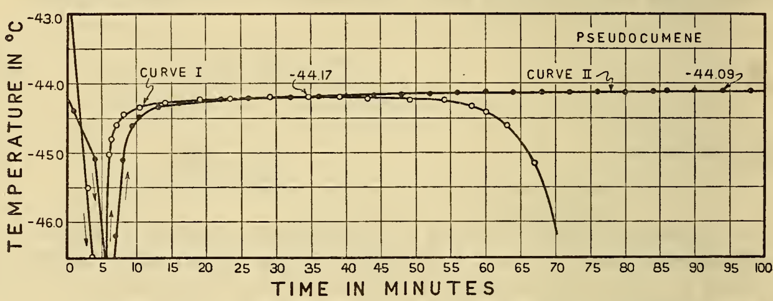

FIGURE 4.—*Time-temperature cooling curves for pseudocumene.*

0.2° C. were obtained in an individual experiment. The pseudocumene supercooled 6° or 7° C. and was very viscous at its freezing temperature. Presumably, equilibrium between the crystals and liquid was not readily attained. The fluctuations in temperature were found to depend on the rate of stirring; by stirring rapidly and uniformly the fluctuations were very much reduced and satisfactory freezing curves obtained. Curve *I*, figure 4, shows the freezing behavior when the vacuum-jacketed tube was immersed in carbon dioxide slush at −78° C. Crystallization of the pseudocumene was induced 4° C. below the freezing point by insertion of a brass rod cooled with liquid air. The maximum temperature attained, −44.17° C., occurred 32 minutes after the initiation of crystallization. At this time the pseudocumene was so nearly solid that stirring was difficult and was stopped about 4 minutes later. It seems probable that the true freezing point was not attained. Curve *II* shows the freezing behavior when the tube was immersed in *n*-nonane slush at −55° C. The maximum temperature attained in this instance was −44.09° C. The temperature was constant within 0.02° C. from the 54th to the 100th minute. In determining the boiling point two thirds of the sample was found to distil over within 0.03° C.

TABLE 2.—*Physical constants of pseudocumene*

Reference	Density at 20° C.	Refractive index n_D^{25}	Boiling point 760 mm	Freezing point in air
	g/ml		° *C.*	° *C.*
Mair and Schicktanz from petroleum	0.8762	1.5025	169.18	−44.09
Smith and Lund (18)		[1] 1.5027	169.1	−45.00
Smith and Cass (16)		[1] 1.5024		
Richards and Barry (19)			169.27	
von Auwers (20)	.876	[1] 1.5021	168.7–169.2	

[1] Corrected to 25° C., assuming $\frac{dn_D}{dt} = 0.0005$.

VIII. PURIFICATION OF MESITYLENE

The mesitylene separated by hydrolysis (*G*, fig. 3) was purified first by the method of Smith and Cass (16), that is, by crystallization of the sulphonic acid from cold 20 percent hydrochloric acid, followed by hydrolysis of the sulphonic acid with constant-boiling hydrochloric acid at 80° C. The mesitylene was then washed, dried, and distilled from sodium. In this manner 308 ml with $n_D^{25}=1.4962$ was obtained. The freezing behavior showed that this material was not quite pure. After two crystallizations from a 50 percent solution in dimethyl ether a very pure sample was obtained. The dimethyl ether was removed by refluxing the mesitylene in a long-necked flask for a few minutes.

IX. PHYSICAL CONSTANTS OF MESITYLENE

Values of certain physical constants of mesitylene isolated from petroleum, determined in the same manner as those of pseudocumene, are compared in table 3 with values for synthetic material obtained by different observers. The material prepared by White and Rose (11) of this Bureau was obtained by condensation of acetone with sulphuric acid, and purified by fractional distillation in an efficient fractionating column and by fractional crystallization from dichlorodifluoromethane. The agreement between the values for the synthetic sample of White and Rose (11) and that from petroleum is excellent and leaves no question as to the identity of the hydrocarbon from petroleum. The slightly lower freezing point indicates that the synthetic sample was somewhat less pure than that from petroleum.

TABLE 3.—*Physical constants of mesitylene*

Reference	Density at 20° C.	Refractive index n_D^{25}	Boiling point 760 mm	Freezing point in air
	g/ml		° *C.*	° *C.*
Mair and Schicktanz from petroleum	0.8653	1.4967	164.64	(α) −44.78 (β) −51.74
White and Rose (11)	.8654	1.4967	164.65	(α) −44.83 (β) −51.83
Richards and Barry (19)			164.72	
Richards and Shipley (21)	.8634			
Maas and Russell (22)			164.5	−53.5
von Auwers (20)	.862	[1] 1.4942	165–166	
Smith and Cass (16)		[1] 1.4949		

[1] Corrected to 25° C., assuming $\frac{dn_D}{dt} = 0.0005$.

X. CRYSTALLINE MODIFICATIONS OF MESITYLENE

It was found that mesitylene had two crystalline modifications, as shown by the time-temperature cooling curves in figures 5 and 6. When the sample was cooled while stirring in the ordinary manner, the lower-freezing (β) modification was obtained. When, however, a brass rod cooled with liquid air was inserted in the freezing tube between $-44.78°$ and $-51.74°$ C. the higher freezing (α) modification resulted.

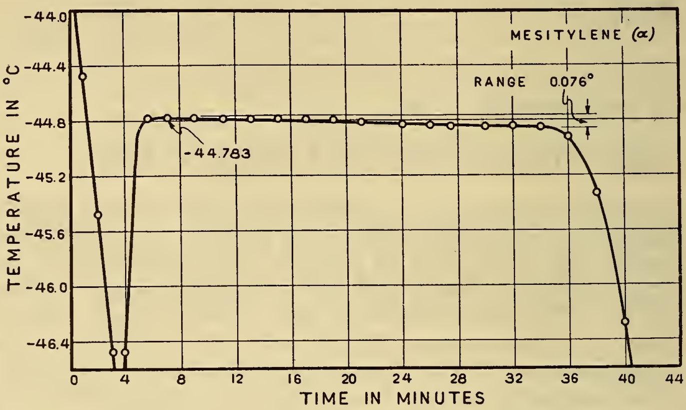

FIGURE 5.—*Time-temperature cooling curve for mesitylene (α form).*

The purity of the mesitylene was calculated on the assumption that the freezing point of pure mesitylene was higher than the initial freezing point of this sample by an amount equal to the difference between the initial freezing temperature and the temperature when half the sample was frozen. For the latent heat of fusion of the α modification the value 2,280 g-cal.$_{15}$ per mole, obtained by Rossini (15) was used. The purity of the mesitylene calculated in this manner was 99.95 mole percent.

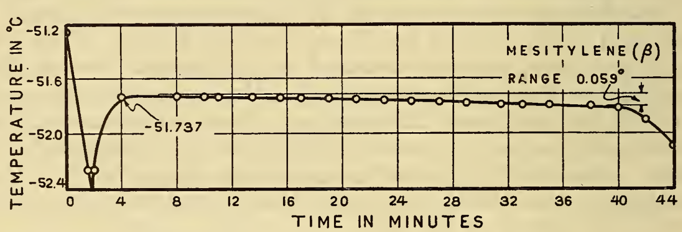

FIGURE 6.—*Time-temperature cooling curve for mesitylene (β form).*

XI. ISOLATION OF HEMIMELLITENE

The letters *A*, *B*, *C*, etc., throughout the following description refer to figure 7 which shows diagrammatically the isolation of hemimellitene. The fractions which distilled between 128° and 132° C. crystallized readily (*A*). These fractions were combined in two portions according to refractive indices (*B*). One portion with refractive index above 1.50 was crystallized from a solution containing 30 to 40 percent of dimethyl ether (*C*) and yielded pure hemimellitene. The

other portion with refractive index below 1.50 was extracted again after admixture of petroleum ether (*D*) in a manner similar to that described for pseudocumene. The extract was fractionally distilled and the distillates combined according to whether their refractive indices were above or below 1.50 (*E*). The portion with refractive index

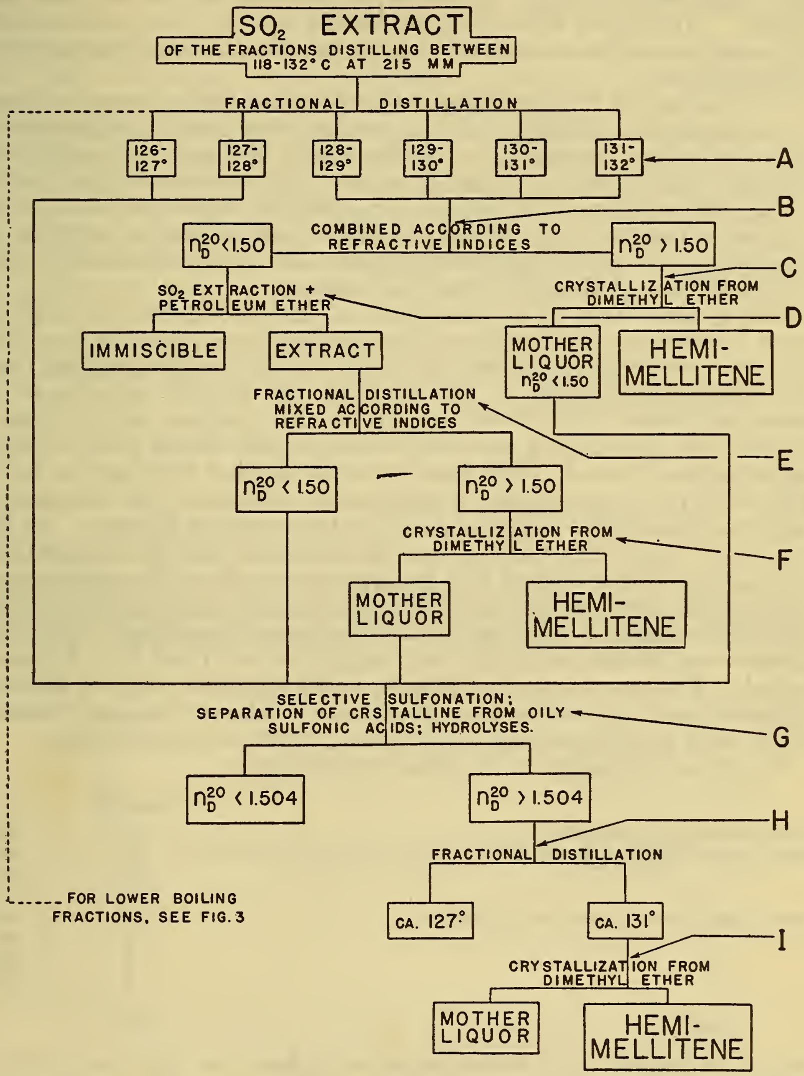

FIGURE 7.—*Chart showing the steps in the isolation of hemimellitene.*

above 1.50 yielded a further sample of hemimellitene on crystallization from dimethyl ether (*F*). When the freezing points of the mother liquors became so low that the use of a centrifuge at the temperatures of solid carbon dioxide was no longer feasible, it was decided to continue the separation by sulphonation and hydrolysis.[6]

[6] Although only solid carbon-dioxide slush was used in the centrifuge jacket, liquid air was used to crystallize the fraction. The effective range of the centrifuge was thus increased somewhat.

Preliminary experiments showed that hemimellitene sulphonates about as readily as pseudocumene. White crystals were obtained when the sulphonated product was run into ice. The hydrolysis of the sulphonic acid from a sulphuric-acid solution was just detectable at 110° C. and progressed with fair speed at 120° to 125° C. It was not rapid until 130° C. Yields of 90 percent and better were obtained. Hydrolysis with constant-boiling hydrochloric acid at 110° C. was also tried but was too slow to be practical, the rate being about 1 ml per hour.

On shaking the hemimellitene mother liquors with an equal volume of concentrated sulphuric acid, a portion was readily sulphonated. There remained, however, a portion which was not so readily sulphonated and which, judging from its high refractive index (n_D^{20}= 1.475), still contained aromatics. On running the sulphonated product into a beaker of ice, white crystals appeared, but in addition to the crystals an oily sulphonated product also appeared which floated on the surface of the sulphuric-acid mixture.

The greater ease of sulphonation of hemimellitene, the slightly lower hydrolysis temperature of the sulphonic acid, and the fact that it forms a crystalline sulphonic acid were utilized in its separation from the other constituents of the fraction. A typical experiment is described below. A 215 ml sample of the fraction (n_D^{20}=1.4944–1.4981) was placed in a one-liter 3-necked flask fitted with a stirrer and dropping funnel. The flask was surrounded with an ice bath. The stirrer was started and concentrated sulphuric acid dropped in slowly, a total of 221 ml being added in the course of 8 hours. At the end of 13 hours, the stirring was discontinued and the contents of the flask were transferred to a separatory funnel. The sulphonated product was run into an approximately equal volume of ice, a white precipitate together with an oily sulphonic acid resulting. The precipitate was filtered with suction through a cloth filter on a Büchner funnel. The precipitate was pressed down to get as much of the oily sulphonic acid as possible into the filtrate. The crystals and mother liquor were hydrolyzed separately from sulphuric-acid solutions.

There were obtained in the above experiment:

	Volume, ml	n_D^{20}
Unsulphonated hydrocarbon	87	1. 4888
From the crystals by hydrolysis	15	1. 5097
	64	1. 5081
	5	1. 5068
From the mother liquors by hydrolysis	3	[1] 1. 4871
	17	1. 5021
	8	1. 4964
	4	1. 5045
Total	203	

In the hydrolysis, the temperature was kept at 120° to 125° C. until practically no more sulphonic acid hydrolyzed, then the temperature was slowly raised to 180° C. In every case, a very small amount of highly refractive material came over at a high temperature. A possible explanation for this is that a second hemimellitenesulphonic acid, hydrolizing at a higher temperature than the first, is formed in small quantities. The entire fraction distilling from 126°

[1] Unsulphonated.

to 132° C. was treated in this manner (*G*). This included the hemimellitene mother liquors and some material in the region from 127° to 128° C. which it had not been possible to crystallize. The lower fractions around 126° C. contained some pseudocumene also. The fractions were collected according to refractive index and those with a refractive index below 1.504 were treated again in the manner just described.

The identification of the material with low refractive index has not been completed. It is suspected, however, that it contains either isobutylbenzene or secondary butylbenzene.

The material with refractive index above 1.504 was fractionally distilled at 215 mm and separated into two fractions, one distilling around 127° C., substantially pseudocumene, and the other distilling around 131° C., substantially hemimellitene (*H*). The hemimellitene was further purified by fractional crystallization from dimethyl ether (*I*). The dimethyl ether was removed by refluxing the hemimellitene for a few minutes in a long-necked flask. The amount isolated is recorded in table 4.

TABLE 4.—*Hemimellitene isolated from petroleum*

Lot	Volume	Refractive index n_D^{25}	Freezing point in air	Purity [1]
	ml		° *C.*	*Mole per cent*
I	280	1.5116	−25.47	99.95
II	510	1.5115	−26.21	98.75
III	80	1.5062	−51	62

[1] The purity of the hemimellitene was calculated from equation 47, p. 203, E. W. Washburn, Principles of Physical Chemistry, McGraw-Hill Book Co., 1921. For the heat of fusion the value 2,000 g-cal[15] per mole obtained by F. D. Rossini (15) was used. The freezing point of pure hemimellitene was assumed to be higher than the initial freezing point of the best sample by an amount equal to the difference between the initial freezing point of this sample and the temperature when half the sample was frozen.

Figure 8 shows the time-temperature cooling curve obtained on hemimellitene.

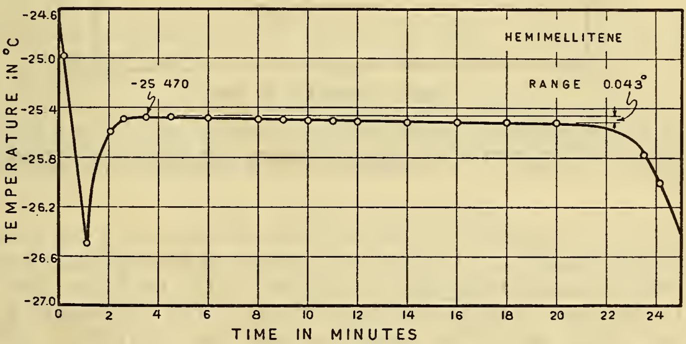

FIGURE 8.—*Time-temperature cooling curve for hemimellitene.*

XII. PHYSICAL CONSTANTS OF HEMIMELLITENE

The physical constants of hemimellitene were determined in a manner similar to that employed with mesitylene and pseudocumene. These constants are recorded in table 5 together with values reported by von Auwers (20). Judging from the boiling range, the sample of

13317—33——8

von Auwers was not pure and the agreement consequently is as good as could be expected. At least there is no question as to the identity of the hydrocarbon from petroleum, since all the other aromatic hydrocarbons boiling near 176° C. have much lower densities and refractive indices.

TABLE 5.—*Physical constants of hemimellitene*

Reference	Density at 20° C.	Refractive index n^{25}_D	Boiling point 760 mm	Freezing point in air
	g/ml		° *C.*	° *C.*
Mair and Schicktanz from petroleum	0.8951	1.5116	176.10	−25.47
von Auwers (20)	.895	[1] 1.5107	175.8–176.8	

[1] Corrected to 25° C., assuming $\frac{dn_D}{dt}=0.0005$.

XIII. INFRARED ABSORPTION SPECTRA OF THE TRIMETHYLBENZENES

Transmission curves of the three trimethylbenzenes at the wave numbers indicated on the graphs (figs. 9 and 10) were obtained from

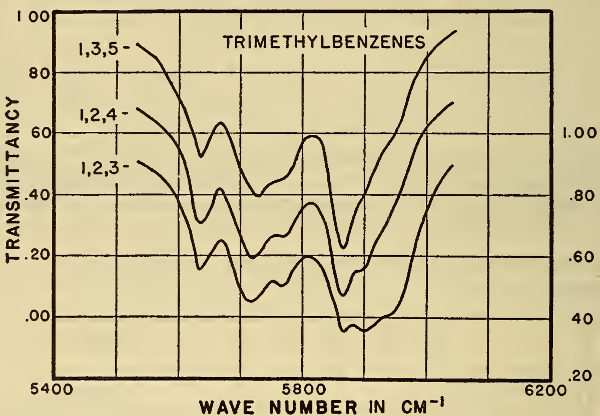

FIGURE 9.—*Transmittancy of the trimethylbenzenes from 5,400 to 6,200 cm⁻¹.*

The ordinate scale on the left refers to 1-, 3-, 5-trimethylbenzene, while that on the right refers to 1-, 2-, 3-trimethylbenzene. The scale for 1-, 2-, 4-trimethylbenzene is intermediate and is displaced 0.2 from the others.

records of the absorption of the compounds through 5 cm of carbontetrachloride solution. The concentrations of mesitylene, pseudocumene and hemimellitene for the region 5,400 to 6,200 cm^{-1} were 0.718, 0.728, and 0.742 molar, respectively. For the region 8,100 to 8,900 cm^{-1} their respective concentrations were 0.1436, 0.1456, and 0.1484 molar. Absorption in the region 5,400 to 6,200 cm^{-1} has been assigned as the first overtone of the absorption of the *C—H* linkage around 2,900 cm^{-1}, and that between 8,100 and 8,900 cm^{-1} as the second overtone of the same band. The band near 8,700 cm^{-1} is to be attributed to the nuclear *C—H* linkages and that around 8,400 cm^{-1} to the side chains. These curves were obtained by U. Liddel, of the Bureau of Chemistry and Soils, and Charles Kasper, of the

Bureau of Standards. A further discussion of these bands and correlations with other hydrocarbons will appear shortly in a paper by Liddel and Kasper.

XIV. CONTENT OF THE TRIMETHYLBENZENES IN THE CRUDE PETROLEUM

Based upon the total amount of the crude petroleum used (600 gallons of specific gravity 0.9) and making reasonable allowances for losses during fractionation, it is estimated that the amounts of pseudocumene and hemimellitene in the crude petroleum are about 0.2 and 0.06 percent, respectively.

The amount of mesitylene in the fraction extracted was about 0.02 percent of the crude petroleum. Since the extraction was carried only as far as the fractions distilling 2° C. below the boiling point of mesitylene, it is possible that more mesitylene will be found in the

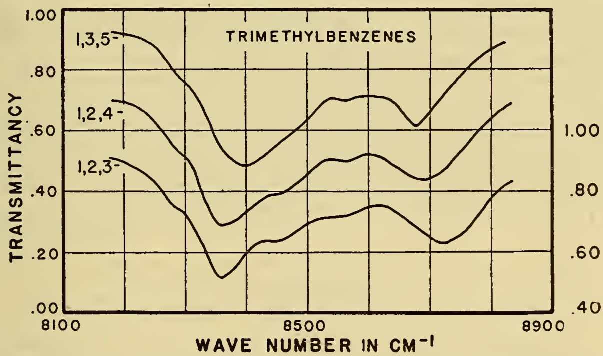

FIGURE 10.—*Transmittancy of the trimethylbenzenes from 8,100 to 8,900 cm*$^{-1}$.

The ordinate scale on the left refers to 1-, 3-, 5-trimethylbenzene, while that on the right refers to 1-, 2-, 3-trimethylbenzene. The scale for 1-, 2-, 4-trimethylbenzene is intermediate and is displaced 0.2 from the others.

fractions immediately below that extracted. Until these fractions have been investigated, the value, 0.02 percent, should be regarded as tentative.

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